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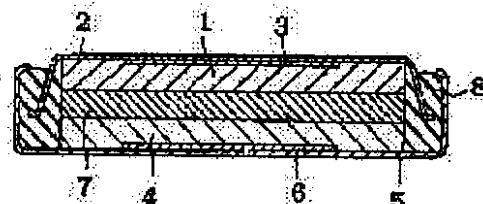
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## (54) NON-AQUEOUS ELECTROLYTE SECONDARY BATTERY

## (57)Abstract:

PURPOSE: To maintain a high discharging capacity, and to improve the cycle characteristic by mixing the lithium compound with  $\text{LiMnO}_4$ , and heat-treating this mixture within a specified temperature range to form the positive electrode active material.

CONSTITUTION: The mixture of lithium compound with  $\text{LiMn}_2\text{O}_4$  is heat-treated within a temperature range at  $400\text{--}1325^\circ\text{C}$  to obtain the complex of lithium- manganese oxide and  $\text{Li}_2\text{MnO}_3$  having the spinel structure. A positive electrode 4 having this complex as the positive electrode active material, a negative electrode 1 having lithium as the active material thereof, the non-aqueous electrolyte and a separator 7 are provided to form a secondary battery. A battery having the excellent cycle characteristic is thereby obtained.



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## CLAIMS

## [Claim(s)]

[Claim 1] The nonaqueous electrolyte rechargeable battery with which the lithium-manganic acid ghost which has said spinel type structure, and the complex of  $\text{Li}_2\text{MnO}_3$  are characterized by heat-treating and obtaining the mixture of a lithium compound and  $\text{LiMn}_2\text{O}_4$  in a 400 degrees C - 1325 degrees C temperature requirement in the nonaqueous electrolyte rechargeable battery equipped with the positive electrode which uses as positive active material the negative electrode which uses a lithium as an active material, a nonaqueous electrolyte, and the lithium-manganic acid ghost which has spinel type structure and the complex of  $\text{Li}_2\text{MnO}_3$ .

[Claim 2] The nonaqueous electrolyte rechargeable battery according to claim 1 characterized by performing heat treatment of said mixture in a 850 degrees C - 950 degrees C temperature requirement.

[Claim 3] The nonaqueous electrolyte rechargeable battery according to claim 1 with which the mixing ratio of said lithium compound and  $\text{LiMn}_2\text{O}_4$  is characterized by being 0.02-0.70 in the Li/Mn atomic ratio of the lithium in said lithium compound, and the manganese in  $\text{LiMn}_2\text{O}_4$ .

[Claim 4] the total in the lithium-manganic acid ghost which has said spinel type structure, and the complex of  $\text{Li}_2\text{MnO}_3$  -- the nonaqueous electrolyte rechargeable battery according to claim 1 with which a Li/Mn atomic ratio is characterized by being 0.52-1.20 in the condition before receiving the extract of a lithium, and insertion electrochemically.

[Claim 5] The nonaqueous electrolyte rechargeable battery according to claim 1 with which said lithium compound is characterized by being a lithium hydroxide.

[Claim 6] The manufacture approach of the positive active material for nonaqueous electrolyte rechargeable batteries characterized by heat-treating said mixture in a 400 degrees C - 1325 degrees C temperature requirement after mixing  $\text{LiMn}_2\text{O}_4$  with a lithium compound and obtaining mixture.

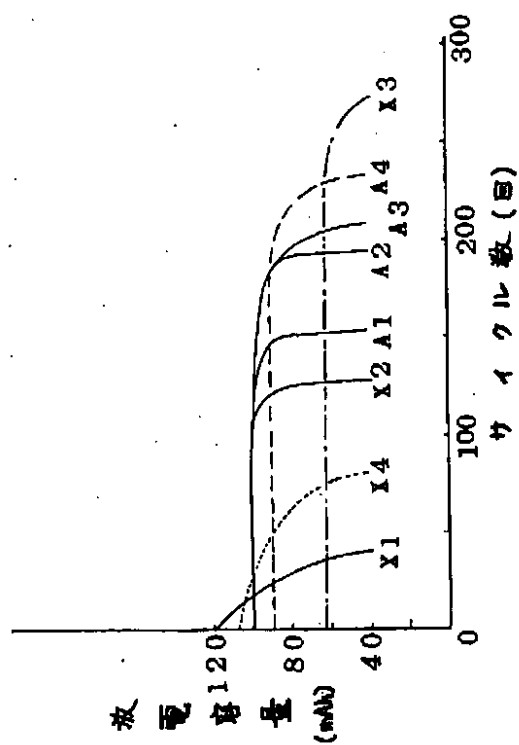
[Claim 7] The manufacture approach of the positive active material for nonaqueous electrolyte rechargeable batteries according to claim 6 characterized by performing heat treatment of said mixture in a 850 degrees C - 950 degrees C temperature requirement.

[Claim 8] The manufacture approach of the positive active material for nonaqueous electrolyte rechargeable batteries according to claim 6 that the mixing ratio of said lithium compound and said  $\text{LiMn}_2\text{O}_4$  is characterized by being referred to as 0.02-0.70 in the Li/Mn atomic ratio of the lithium in said lithium compound, and the manganese in said  $\text{LiMn}_2\text{O}_4$ .

[Claim 9] The manufacture approach of the positive active material for nonaqueous electrolyte rechargeable batteries according to claim 6 characterized by obtaining the lithium-manganic acid ghost which heat-treats said mixture and has spinel type structure, and complex with  $\text{Li}_2\text{MnO}_3$ , and setting all the Li/Mn atomic ratios in said complex to 0.52-1.20.

[Claim 10] The manufacture approach of the positive active material for nonaqueous electrolyte rechargeable batteries according to claim 6 that said lithium compound is characterized by being a lithium hydroxide.

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[Translation done.]

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to amelioration of the positive active material aiming at improvement in a charge-and-discharge cycle property especially with respect to the nonaqueous electrolyte rechargeable battery which uses a manganic acid ghost as positive active material.

[0002]

[Description of the Prior Art] Conventionally, the lithium-manganic acid ghost which has spinel type structure which was indicated by JP,4-30146,B from the reason of being able to take out the high voltage ( $\text{LiMn}_2\text{O}_4$ ), i.e., the lithium-manganic acid ghost expressed with general formula  $\text{Li}_{1-X}\text{Mn}_2\text{O}_4$  ( $0 \leq X \leq 1$ ), is studied as positive active material of a nonaqueous electrolyte rechargeable battery. However, since manganese was eluted at the time of the charge to which a positive electrode serves as high potential, the lithium-manganic acid ghost which has this spinel type structure had the problem that a cycle property was not fully acquired.

[0003] this invention person etc. sets to Japanese Patent Application No. No. 280469 [ four to ] that this problem should be solved. By mixing with a lithium hydroxide ( $\text{LiOH}$ ) the lithium-manganic acid ghost ( $\text{LiMn}_2\text{O}_4$ ) which has spinel type structure, and heat-treating at 375 degrees C Three layer of  $\text{Li}_2\text{MnO}_3$  were formed in the front face of the lithium-manganic acid ghost ( $\text{Li}_{1-X}\text{Mn}_2\text{O}_4$ ;  $0 \leq X \leq 1$ ) particle which has spinel type structure, and the technique which raises a cycle property is proposed. Although surely a cycle property will improve if the ratio of the lithium hydroxide to mix is made high so that drawing 3 of this application may see, there is a new problem that discharge capacity falls.

[0004]

[Problem(s) to be Solved by the Invention] Then, learning of a cell property changing was carried out by changing the heat treatment temperature of the mixture which consists of a lithium-manganic acid ghost which has spinel type structure, and a lithium hydroxide as a result of this invention person's examination. That is, a cycle property is further raised by heat-treating mixture in a specific temperature requirement. Furthermore, improvement in a cycle property is aimed at, maintaining a high discharge capacity.

[0005]

[Means for Solving the Problem] This invention is the nonaqueous electrolyte rechargeable battery equipped with the positive electrode which uses as positive active material the negative electrode which uses a lithium as an active material, a nonaqueous electrolyte, and the lithium-manganic acid ghost which has spinel type structure and the complex of  $\text{Li}_2\text{MnO}_3$ , and complex is characterized by heat-treating and obtaining the mixture of a lithium compound and  $\text{LiMn}_2\text{O}_4$  in a 400 degrees C - 1325 degrees C temperature requirement.

[0006] Moreover, after the manufacture approach of the positive electrode for nonaqueous electrolyte rechargeable batteries of this invention mixes  $\text{LiMn}_2\text{O}_4$  with a lithium compound and obtains mixture, it is characterized by heat-treating said mixture in a 400 degrees C - 1325 degrees C temperature requirement.

[0007] Here, it is desirable from a viewpoint of a cycle property and discharge capacity to make heat treatment of mixture into a 850 degrees C - 950 degrees C temperature requirement especially.

[0008] And the mixing ratio of a lithium compound and  $\text{LiMn}_2\text{O}_4$  should be made 0.02-0.70 in the Li/Mn atomic ratio of the lithium in said lithium compound, and the manganese in said  $\text{LiMn}_2\text{O}_4$ .

[0009] moreover, the total in the lithium-manganic acid ghost which has said spinel type structure, and the complex of  $\text{Li}_2\text{MnO}_3$  -- a Li/Mn atomic ratio is characterized by being referred to as 0.52-1.20 in the condition before receiving the extract of a lithium, and insertion electrochemically.

[0010] Here, as a lithium compound which mixes with  $\text{LiMn}_2\text{O}_4$  and is heat-treated, water-of-hydration lithium

oxide ( $\text{LiOH} \cdot \text{H}_2\text{O}$ ), a lithium carbonate ( $\text{Li}_2\text{CO}_3$ ), lithium oxide ( $\text{Li}_2\text{O}$ ), a lithium nitrate ( $\text{LiNO}_3$ ), etc. can be used in addition to a lithium hydroxide ( $\text{LiOH}$ ). the case where a lithium hydroxide ( $\text{LiOH}$ ) is used especially -- a lithium hydroxide -- this seed production process -- setting -- stable -- acquisition -- it is easy, and since the reactivity at the time of heat treatment is high, it is suitable. Moreover,  $\text{LiMn}_2\text{O}_4$  used as the secondary raw material of this positive active material is the compoundable matter easily, and especially that synthesis method is not limited.

[0011] As a solvent of this invention cell, as an usable solvent, for example, propylene carbonate (PC), Ethylene carbonate (EC), butylene carbonate (BC), vinylene carbonate (VC), Gamma-butyrolactone (gamma-BL), dimethyl carbonate (DMC), Diethyl carbonate (DEC), methylethyl carbonate (MEC), Dimethoxyethane (DME), tetrahydrofuran (THF), dioxolane (DOXL), 1, and 2-diethoxy ethane (DEE) etc. can be used, and these mixed solvents are usable suitably according to a cell design.

[0012] Moreover, as an usable solute, although  $\text{LiCF}_3\text{SO}_3$ , and  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$  and  $\text{LiClO}_4$  can be mentioned, if the property of a rechargeable battery is taken into consideration,  $\text{LiPF}_6$  and especially  $\text{LiCF}_3\text{SO}_3$  are desirable.

[0013] Furthermore, carbon materials, such as a lithium alloy or a graphite, may be used in addition to the lithium metal which is the ingredient which can emit [ occlusion and ] the lithium as an active material as a negative electrode of this seed cell.

[0014]

[Function] Since the conjugated compound which has structure in which three layer of  $\text{Li}_2\text{MnO}(\text{s})$  covered with this invention the front face of a lithium-manganic acid ghost ( $\text{LiMn}_2\text{O}_4$ ) particle where positive active material has spinel type structure is used, the area which  $\text{LiMn}_2\text{O}_4$  in positive active material contacts directly decreases, and it is considered the electrolytic solution because the elution of Mn is controlled from  $\text{LiMn}_2\text{O}_4$  at the time of charge. If this conjugated compound is analyzed by X-ray diffraction, it is checked rather than what consists of a mere mixture of the lithium-manganic acid ghost ( $\text{LiMn}_2\text{O}_4$ ) particle which has spinel type structure, and  $\text{Li}_2\text{MnO}_3$  particle that the near diffraction peak has shifted [ whenever / angle-of-elevation / of the lithium-manganic acid ghost ( $\text{LiMn}_2\text{O}_4$ ) which has spinel type structure ] to a side whenever [ angle-of-elevation ] more. The above-mentioned conjugated compound is not mere mixture but the compound-ized proof, and this is the description of the positive active material of this invention.

[0015] And they are a lithium [ with which positive active material both has the 375 degrees C of the 400 degrees C of the same spinel type structures as a crystal structure about heat treatment temperature ]-manganic acid ghost ( $\text{LiMn}_2\text{O}_4$ ), and complex with  $\text{Li}_2\text{MnO}_3$ . In the lithium-manganic acid ghost ( $\text{LiMn}_2\text{O}_4$ ) which has spinel type structure when heat treatment temperature becomes 400 degrees C or more, and complex with  $\text{Li}_2\text{MnO}_3$  three layer of  $\text{Li}_2\text{MnO}(\text{s})$  of a positive-active-material particle front face more Homogeneity and since it becomes precise, The work which protects the lithium-manganic acid ghost ( $\text{LiMn}_2\text{O}_4$ ) which has the spinel type structure inside a particle acts more effectively, and is considered that the work which raises a cycle property will increase.

[0016] On the other hand, as an upper limit of heat treatment temperature, when it is made 1400 degrees C, it is checking that a cycle property is good. However, if it says from a viewpoint of \*\* et al. and discharge capacity, it cannot be said that it is desirable. It is guessed that this reason is because a part of lithium-manganic acid ghost ( $\text{LiMn}_2\text{O}_4$ ) which has the spinel type structure in positive active material has understood. If analysis according the positive active material heat-treated at such an elevated temperature to an X diffraction is carried out, existence of  $\text{Mn}_3\text{O}_4$  presumed to be a decomposition product is checked.

[0017] And by the cell using the positive active material which made heat treatment temperature 1325 degrees C, although a cycle property is good, discharge capacity falls a little. In this temperature, three layer of  $\text{Li}_2\text{MnO}(\text{s})$  on the front face of positive active material progress too much, and this reason is considered to be for the inclination to block the electrode reaction of the lithium-manganic acid ghost ( $\text{LiMn}_2\text{O}_4$ ) and the electrolytic solution which have the spinel type structure inside an active material particle to come out. Therefore, the upper limit of heat treatment should be made even this temperature.

[0018] In addition, also when it mixes with 0.5 or more mixing ratios in a Li/Mn atomic ratio and a lithium compound and a manganese compound are calcinated at the temperature of about 500 degrees C or more, the complex of the lithium-manganic acid ghost ( $\text{LiMn}_2\text{O}_4$ ) which has  $\text{Li}_2\text{MnO}_3$  and spinel type structure generates. The complex obtained by such approach serves as structure to which the  $\text{Li}_2\text{MnO}_3$  crystal layer and the crystal layer of a spinel mold were intermingled at random in the particle. Therefore, it is the last structure by which the lithium-manganic acid ghost ( $\text{LiMn}_2\text{O}_4$ ) which has spinel type structure which is made into the object of this invention would exist in the interior of a particle, and  $\text{Li}_2\text{MnO}_3$  would be alternatively formed in the particle front face in the shape of a layer. Consequently, since three layer of  $\text{Li}_2\text{MnO}(\text{s})$  are deficient in the effectiveness of

decreasing the touch area of 2O4 layer of LiMn(s), and the electrolytic solution, about the point which also raises a cycle property, maintaining a high discharge capacity, it is inferior to the thing of the invention in this application.

[0019]

[Example] Below, it explains about the example of this invention.

(Example 1)

(Production of a positive electrode) The lithium hydroxide (LiOH) and manganese dioxide which are a start ingredient were mixed so that it might become the mole ratio of Li:Mn=1:2, mixture was obtained, it calcinated at 850 degrees C among air for 20 hours, and LiMn 2O4 was obtained. These 2O4 1 mol of LiMn(s) and 0.2 mols (LiOH) of lithium hydroxides were mixed, it heat-treated at 400 degrees C among air for 20 hours, and complex was obtained. When a mixing ratio here is expressed by the Li/Mn atomic ratio of the lithium in a lithium hydroxide (LiOH), and the manganese in LiMn 2O4, it is 0.1.

[0020] When X diffraction measurement of the obtained complex is carried out and it collates with a JSPDS card, the diffraction line of LiMn 2O4 and Li2MnO3 is accepted, and it is checked that especially LiMn 2O4 has spinel type structure. And it is thought that the particulate structure of this complex is the composite particle by which three layer of Li2MnO(s) were formed in the front face of the lithium manganic acid ghost (LiMn 2O4) particle which has spinel type structure. moreover, the total in the complex which consists of a lithium manganic acid ghost (LiMn 2O4) which has this spinel type structure, and Li2MnO3 -- it was 0.60 when the Li/Mn atomic ratio was measured according to atomic absorption analysis.

[0021] thus, the positive active material which is the complex which consists of a lithium manganic acid ghost (LiMn 2O4) which has the acquired spinel type structure, and Li2MnO3, the carbon black as an electric conduction agent, and the fluororesin as a binder -- the weight ratio 85:10:5 -- mixing -- a positive electrode -- the mixture was obtained. this positive electrode -- the mixture was fabricated and the disc-like positive electrode was produced. And further, this positive electrode is dried at 250 degrees C among a vacuum for 20 hours, and it is used for a cell.

[0022] (Production of a negative electrode) The lithium metal was rolled out, was pierced and carried out, and the disc-like negative electrode was produced. In addition, the stainless steel plate (SUS304) was used as a negative-electrode charge collector.

[0023] (Preparation of nonaqueous electrolyte) LiPF6 (hexa fluorophosphoric acid lithium) was melted by the concentration of one mol/l. to volume mixed solvents, such as propylene carbonate (PC) and 1 and 2-dimethoxyethane (DME), and nonaqueous electrolyte was prepared to them.

[0024] [Assembly of a cell] Drawing 1 is the half section Fig. of the flat mold nonaqueous electrolyte cell of this invention example. Among drawing, one is a negative electrode which consists of a lithium metal, and is stuck to the inner base of the negative-electrode can 2 by the fixing \*\*\*\* negative-electrode charge collector 3 by pressure. 4 is a positive electrode which is the main point of this invention, and the pressure welding is carried out to the fixing \*\*\*\* positive-electrode charge collector 6 on the inner base of the positive-electrode can 5. In addition, a stainless steel plate (SUS316) is used as the positive-electrode can 5 and a positive-electrode charge collector 6, and the stainless steel plate (SUS304) is used as a negative electrode 1 and a negative-electrode charge collector 3. 7 is a separator which consists of porosity film made from polypropylene, and the nonaqueous electrolyte adjusted as mentioned above sinks in. 8 is insulating packing, and the dimension of this cell is 3mm in the diameter of 24mm, and height, and uses this cell as this invention cell A1.

(Example 2) In production of the complex which consists of a lithium manganic acid ghost (LiMn 2O4) which has the spinel type structure which is positive active material, and Li2MnO3, if it removed having made into 850 degrees C heat treatment temperature of the mixture which consists of LiMn 2O4 and a lithium hydroxide (LiOH), this invention cell A2 was produced like said example 1.

(Example 3) In production of the complex which consists of a lithium manganic acid ghost which has the spinel type structure which is positive active material, and Li2MnO3, if it removed having made into 950 degrees C heat treatment temperature of the mixture which consists of LiMn 2O4 and a lithium hydroxide, this invention cell A3 was produced like said example 1.

(Example 4) In production of the complex which consists of a lithium manganic acid ghost which has the spinel type structure which is positive active material, and Li2MnO3, if it removed having made into 1325 degrees C heat treatment temperature of the mixture which consists of LiMn 2O4 and a lithium hydroxide, this invention cell A4 was produced like said example 1.

(Example 1 of a comparison) If it removed having used the lithium manganic acid ghost (LiMn 2O4) which has spinel type structure as positive active material, the comparison cell X1 was produced like said example 1.



(Example 2 of a comparison) In production of the complex which consists of a lithium manganic acid ghost (LiMn 2O<sub>4</sub>) which has the spinel type structure which is positive active material, and Li<sub>2</sub>MnO<sub>3</sub>, if it removed having made into 375 degrees C heat treatment temperature of the mixture which consists of LiMn 2O<sub>4</sub> and a lithium hydroxide, the comparison cell X2 was produced like said example 1.

[0025] In addition, this comparison cell X2 is the same as the cell which was explained according to the item of a Prior art and which was indicated by the example 1 of Japanese Patent Application No. No. 280469 [ four to ].

(Example 3 of a comparison) In production of the complex which consists of a lithium manganic acid ghost (LiMn 2O<sub>4</sub>) which has the spinel type structure which is positive active material, and Li<sub>2</sub>MnO<sub>3</sub>, if it removed having made into 1400 degrees C heat treatment temperature of the mixture which consists of LiMn 2O<sub>4</sub> and a lithium hydroxide, the same comparison cell X3 as said example 1 was produced.

(Example 4 of a comparison) In production of the complex which consists of a lithium manganic acid ghost (LiMn 2O<sub>4</sub>) which has the spinel type structure which is positive active material, and Li<sub>2</sub>MnO<sub>3</sub>, one mol (MnO<sub>2</sub>) of manganese dioxides was mixed with 0.6 mols (LiOH) of lithium hydroxides, and if it removed having calcinated this mixture at 850 degrees C among air for 20 hours, the comparison cell X4 was produced like said example 1.

[0026] in addition -- thus, the active material of each cell of the examples 1-4 which obtained by carrying out, and the examples 1-4 of a comparison -- the Li/Mn ratio in a mixing ratio, heat treatment temperature, and a product and the crystal structure of a product are listed to Table 1.

[0027]

[Table 1]

	出発原料混合比 LiOH + LiMn <sub>2</sub> O <sub>4</sub> Li (in LiOH) / Mn (in LiMn <sub>2</sub> O <sub>4</sub> )	Li化合物 + LiMn <sub>2</sub> O <sub>4</sub> 熱処 理温度 (℃)	生成物の Li / Mn比	生成物の 結晶構造
比較例 1	0	なし	0	LiMn <sub>2</sub> O <sub>4</sub>
比較例 2	0 . 2	3 7 5	0 . 6 0	Li <sub>2</sub> MnO <sub>3</sub> + LiMn <sub>2</sub> O <sub>4</sub>
実施例 1	0 . 2	4 0 0	0 . 6 0	Li <sub>2</sub> MnO <sub>3</sub> + LiMn <sub>2</sub> O <sub>4</sub>
実施例 2	0 . 2	8 5 0	0 . 6 0	Li <sub>2</sub> MnO <sub>3</sub> + LiMn <sub>2</sub> O <sub>4</sub>
実施例 3	0 . 2	9 5 0	0 . 6 0	Li <sub>2</sub> MnO <sub>3</sub> + LiMn <sub>2</sub> O <sub>4</sub>
実施例 4	0 . 2	1 3 2 5	0 . 6 0	Li <sub>2</sub> MnO <sub>3</sub> + LiMn <sub>2</sub> O <sub>4</sub>
比較例 3	0 . 2	1 4 0 0	0 . 6 0	Li <sub>2</sub> MnO <sub>3</sub> + LiMn <sub>2</sub> O <sub>4</sub>
比較例 4	0 . 6 $\frac{\text{Li (in LiOH)}}{\text{Mn (in MnO}_2\text{)}}$	8 5 0 (LiOH + MnO <sub>2</sub> )	0 . 8 0	Li <sub>2</sub> MnO <sub>3</sub> + LiMn <sub>2</sub> O <sub>4</sub>

[0028] (Cycle trial) About this invention cell A1 - A4, and the comparison cells X1-X4, the bottom of a room temperature (25 degrees C), and after charging to 4.5V by 3mA, the cycle trial which makes 1 cycle the process which discharges to 3.0V by 3mA was performed, and the cycle property of each cell was investigated. This result is shown in drawing 2. Drawing 2 is drawing showing the relation of the number of charge-and-discharge cycles (time) and discharge capacity (mAh) of this invention cell A1 - A4, and the comparison cells X1-X4.

[0029] It turns out that the cycle property of the comparison cell [ using the complex which consists of a lithium manganic acid ghost (LiMn 2O<sub>4</sub>) which has spinel type structure from drawing 2 compared with the comparison cell X1 using only the lithium manganic acid ghost (LiMn 2O<sub>4</sub>) which has spinel type structure as positive active material, and Li<sub>2</sub>MnO<sub>3</sub> as positive active material ] X2 is improving a little. Since this is having structure with which three layer of Li<sub>2</sub>MnO(s) covered the front face of a lithium manganic acid ghost (LiMn 2O<sub>4</sub>) particle where positive active material has spinel type structure, the area which the lithium manganic acid ghost which has the spinel type structure in the electrolytic solution and positive active material contacts directly decreases, and it is

considered to be because for the elution of the manganese from the lithium manganic acid ghost which has spinel type structure at the time of charge to be controlled.

[0030] And by this invention cell A1, the cycle property is improving further compared with the comparison cell X2. Although the positive active material used for this comparison cell X2 and this invention cell A1 is complex which consists of a lithium manganic acid ghost (LiMn 2O4) which both has the same complex, i.e., spinel type structure, as a crystal structure, and Li2MnO3, that production temperature is 375 degrees C by the comparison cell X2, and makes it 400 degrees C by this invention cell A1. Since three layer of Li2MnO(s) of a positive-active-material particle front face of the one where the production temperature of the complex which consists of a lithium manganic acid ghost (LiMn 2O4) which has spinel type structure, and Li2MnO3 is higher than this are more uniform and it becomes precise, although LiMn 2O4 inside a particle is protected, it is thought that the work which raises the cycle property of the lithium manganic acid ghost (LiMn 2O4) which has spinel type structure will increase.

[0031] Furthermore, in this invention cell A2 and A3 which obtained to 850 degrees C, 950 degrees C, and an elevated temperature by carrying out production temperature of the complex which consists of a lithium manganic acid ghost (LiMn 2O4) which has spinel type structure, and Li2MnO3, a cycle property also improves further, maintaining a high discharge capacity. This reason is guessed as follows. That is, although three layer of Li2MnO(s) of the positive-active-material particle front face which is the complex which consists of a lithium manganic acid ghost (LiMn 2O4) which has spinel type structure, and Li2MnO3 by this temperature requirement have become uniform and precise, three layer of Li2MnO(s) are moderately developed, and it is thought that it is for not checking electrode reaction of the lithium manganic acid ghost (LiMn 2O4) and the electrolytic solution which have the spinel type structure inside an active material particle.

[0032] However, in this invention cell A4 which made production temperature of the complex which consists of a lithium manganic acid ghost (LiMn 2O4) which has \*\* et al. and spinel type structure, and Li2MnO3 1325 degrees C, although the cycle property is good, discharge capacity is falling. At this temperature, three layer of Li2MnO(s) on the front face of positive active material progress too much, and it is thought that it is for blocking the electrode reaction of the lithium manganic acid ghost (LiMn 2O4) and the electrolytic solution which have the spinel type structure inside an active material particle.

[0033] And the production temperature of the complex which consists of a lithium manganic acid ghost (LiMn 2O4) which has spinel type structure, and Li2MnO3 is raised further, and discharge capacity is falling remarkably by the comparison cell X3 which made heat treatment temperature 1400 degrees C. This is considered to be because for the lithium manganic acid ghost (LiMn 2O4) which has the spinel type structure in positive active material to have decomposed.

[0034] moreover, the comparison cell X4 which used as the start ingredient the complex which consists of a lithium manganic acid ghost (LiMn 2O4) which has spinel type structure, and Li2MnO3, and produced and used it by heat treatment of a single step -- setting -- the total in complex -- a Li/Mn ratio is the same as that of this invention cells A1 and A2, and its abundance ratio of Li2MnO3 and LiMn 2O4 is also the same. However, since the Li2MnO three-phase-circuit [ within \*\* et al. and a particle ] and 3O'sLiMn4 phase's existence part is random, it is not the structure where Li2MnO3 exists in a particle front face alternatively like the positive active material used by this invention cell. Therefore, the cycle property of the comparison cell X4 is what was inferior compared with this invention cell A1 - A4.

[0035] As mentioned above, the production approach of the complex which consists of a lithium manganic acid ghost (LiMn 2O4) which has spinel type structure, and Li2MnO3 needs heat-of-mixing processing with a lithium compound and LiMn 2O4. And from a viewpoint of 400 degrees C - 950 degrees C being suitable, and raising a cycle property from a viewpoint of maintaining the discharge capacity of a cell highly as production temperature, i.e., heat treatment temperature, 850 degrees C - 1325 degrees C are suitable. Furthermore, from a viewpoint of both discharge capacity and a cycle property, a 850 degrees C - 950 degrees C temperature requirement is desirable.

[0036] In addition, if the rate of the lithium hydroxide (LiOH) mixed with LiMn 2O4 here is too small, since Li2MnO3 surface layer to generate will become coarsely and thin, protection of internal LiMn 2O4 is not enough, and effectiveness of the improvement in a property cannot be desired. On the other hand, if there are too many mixing ratios of a lithium hydroxide, the amount of generation of Li2MnO3 which does not participate in a charge-and-discharge reaction will become large, and the discharge capacity as positive active material will fall. Therefore, the range of atomic ratio Li/Mn of the lithium in the lithium compound as a raw material and the manganese in LiMn 2O4 of a suitable mixing ratio is 0.02-0.70. the total in the complex which consists of a

lithium manganic acid ghost ( $\text{LiMn}_2\text{O}_4$ ) which has the spinel type structure this [ whose ] is a product, and  $\text{Li}_2\text{MnO}_3$  -- it will be set to 0.52-1.20 if it expresses by the Li/Mn atomic ratio. And  $\text{LiMn}_2\text{O}_4$  used as the start raw material of this positive active material is the compoundable matter easily, and especially that synthesis method is not limited.

[0037]

[Effect of the Invention] As mentioned above, according to this invention, the cycle property of this seed cell was able to be raised. In addition, since improvement in a cycle property can be aimed at maintaining a high discharge capacity, the industrial value is very large.

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[Translation done.]